Supplemental Material for Coherent Electronic Coupling in Atomically Thin MoSe$_2$

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OPTICAL BLOCH EQUATIONS SIMULATIONS

The ultrafast two-dimensional pump-probe spectrum is simulated by analytically solving a perturbative expansion of the optical Bloch equations. The simulations are based on the four-level energy scheme presented in Suppl. Fig. 1. Before discussing details of the simulation, justification for describing the exciton-trion system using a four-level energy scheme is provided, based on the idea of a Hilbert space transformation $S[1]$. Let us consider two independent systems with Hamiltonians $H_1$ and $H_2$, consisting of $m$ and $n$ uncoupled states, respectively. Each Hamiltonian can be written as

$$H_1 = \begin{pmatrix} E_1 & 0 & \cdots & 0 \\ 0 & E_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & E_m \end{pmatrix}, \tag{1}$$

$$H_2 = \begin{pmatrix} E'_1 & 0 & \cdots & 0 \\ 0 & E'_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & E'_n \end{pmatrix}, \tag{2}$$

where the diagonal elements are the energy eigenvalues of the two systems. The two independent systems can be combined through a Hilbert space transformation into a single system with $m \times n$ states and total Hamiltonian $H_{\text{tot}}$ given by

$$H_{\text{tot}} = H_1 \otimes I_n + I_m \otimes H_2, \tag{3}$$

where $I_j$ is the identity matrix of size $j$. $H_{\text{tot}}$ is a diagonal matrix with its diagonal elements equal to the energy eigenvalues of the combined system.

Using this procedure, two independent two-level systems can be represented by an equivalent four-level diamond scheme. Let us consider two non-interacting singly-excited exciton and trion transitions $|g\rangle \leftrightarrow |X\rangle$ and $|g\rangle \leftrightarrow |T\rangle$, respectively, as shown in Suppl. Fig. 1(a).

Supplemental Figure 1. Two independent two-level systems (a) and the equivalent four-level diamond system (b). Similar lines (solid or dashed) indicate the transitions that must have identical properties for the two representations to be equivalent. The states in (b) consist of two-particle states, as explicitly shown in (c).

An equivalent four-level system is shown in Suppl. Fig. 1(b), where $|0\rangle$ is the ground state, $|1\rangle$ and $|2\rangle$ are the trion and exciton states, respectively, and state $|3\rangle$ comprises both the $|X\rangle$ and $|T\rangle$ transitions. These two representations are equivalent provided that the lower transitions, $|0\rangle \leftrightarrow |2\rangle$ and $|0\rangle \leftrightarrow |1\rangle$, have equal values for the electronic and optical properties, such as the resonance energy, dipole moment, and dephasing rate, compared to the corresponding upper transitions, $|1\rangle \rightarrow |3\rangle$ and $|2\rangle \rightarrow |3\rangle$, respectively. The states represented in Suppl. Fig. 1(b) are essentially two-particle states, as indicated in Suppl. Fig. 1(c). For example, the singly-excited states $|2\rangle$ and $|1\rangle$ are the composite states for the exciton-trion system with either the exciton or the trion in the excited state, respectively.

Experimentally, modulation of the pump and probe amplitudes and phase-sensitive detection of the nonlinear pump-probe signal at the modulation difference fre-
frequency isolates quantum mechanical pathways for which the pump field acts twice, the probe field once, and the detected signal comprises the interference between the nonlinear signal and the reflected probe field acting as a local oscillator. Moreover, the experiment is performed so that the pump pulse precedes the probe pulse. All possible quantum pathways for this configuration are represented by the double-sided Feynman diagrams shown in Fig. 2(c) of the main text. Only the quantum pathways for which either the pump or the probe pulse can excite the exciton or trion, but not both simultaneously, are considered, consistent with our experiments. In the experiment, the signal detected at the photodiode consists of the nonlinear signal generated by the pump and probe pulses as well as the reflected probe pulse acting as a local oscillator and is given by

\[ R = |E_{pr} + \Delta E_{pr}|^2 = |E_{pr}|^2 + |\Delta E_{pr}|^2 + E_{pr} \cdot \Delta E_{pr}^* + E_{pr}^* \cdot \Delta E_{pr}, \]  

where \( E_{pr} \) is the reflected probe field and \( \Delta E_{pr} \) is the nonlinear signal field. \( \Delta E_{pr} \) is related to the pump (\( E_p \)) and probe field amplitudes by \( \Delta E_{pr} \propto E_{pr} \cdot E_p \cdot E_{pr}^* \), so that the cross term \( E_{pr}^* \cdot \Delta E_{pr} \) in Suppl. Eqn. 4 is proportional to \( |E_{pr}|^2 \cdot |E_p|^2 \). This term is modulated at the pump-probe modulation frequency \( \Omega_p = 2 \text{ kHz} \), which is detected by the lock-in amplifier, while all other terms are filtered. Thus, to simulate the differential pump-probe signal, \( dR = (R - R_0) / R_0 \), one needs to use the Feynman diagrams given in Fig. 2(c) of the main text to calculate \( \Delta E_{pr} \). \( \Delta E_{pr} \) is calculated in the time domain by perturbatively solving the optical Bloch equations to third order in the applied field using a similar method as in Ref. S[2]. The simulations are performed using Dirac delta function pulses in time with the pump preceding the probe, as depicted in the timing diagram in Suppl. Fig. 2(a). The total nonlinear signal is given by summing contributions from each double-sided Feynman diagram in Fig. 2(c) of the main text. The Feynman diagrams can be generalized into three types of diagrams corresponding to nonlinearities arising from excited state emission (Suppl. Fig. 2(b)), ground state bleaching (Suppl. Fig. 2(c)), and excited state absorption (Suppl. Fig. 2(d)).

A generalized expression for diagrams in Suppl. Figs. 2(a), 2(b), and 2(c) is given by Eqns. (5), (6), and (7), respectively.

\[
\Delta E_{pr} \propto \frac{\mu_{kj}^4}{8\hbar^3} \cdot E_{pr} \cdot E_p \cdot E_{pr}^* \cdot \Theta(t) \cdot \Theta(t_D) \cdot \Theta(\tau) \cdot e^{i(\omega_{kj} \cdot \tau - \omega_{kj} t)} \cdot e^{-(\gamma_{kj} \cdot \tau + \gamma_{pop} \cdot \tau_D + \gamma_{kk} t)} \\
\Delta E_{pr} \propto \frac{\mu_{kj}^2 \mu_{lj}^2}{8\hbar^3} \cdot E_{pr} \cdot E_p \cdot E_{pr}^* \cdot \Theta(t) \cdot \Theta(t_D) \cdot \Theta(\tau) \cdot e^{i(\omega_{kj} \cdot \tau - \omega_{lj} t)} \cdot e^{-(\gamma_{kj} \cdot \tau + \gamma_{pop} \cdot \tau_D + \gamma_{lj} t)}
\]

\[
\Delta E_{pr} \propto \frac{\mu_{kj}^2 \mu_{lj}^2}{8\hbar^3} \cdot E_{pr} \cdot E_p \cdot E_{pr} \cdot \Theta(t) \cdot \Theta(t_D) \cdot \Theta(\tau) \cdot e^{i(\omega_{kj} \cdot \tau - \omega_{lj} t)} \cdot e^{-(\gamma_{kj} \cdot \tau + \gamma_{pop} \cdot \tau_D + \gamma_{lj} t)}
\]

Free parameters for each include the normalized dipole moment (\( \mu \)), homogeneous linewidth full-width at half-maximum (\( \gamma \)), population decay rate (\( \gamma_{pop} \)), and transition energy (\( \hbar \omega \)). Inhomogeneity of the transition energies can be included by integrating each equation over a two-dimensional Gaussian distribution that correlates the transition energies during the first (\( \tau \)) and third (\( t \)) time delays and whose Fourier pairs correspond to the pump and probe frequencies, respectively. Perfect correlation of the transition energies during \( \tau \) and \( t \) implies that any change in the transition energy during \( t \) is correlated with changes in the energy during \( \tau \). For the rephasing quantum pathways for peaks X and T in which the conjugated pump field (\( E_{pr}^* \)) acts on the sample first, perfect correlation results in an elongated peak that is inhomogeneously broadened along the diagonal line connecting similar pump and probe energies (\( \hbar \omega_{pr} = \hbar \omega_{pr} \)) and is narrow along the orthogonal direction with a linewidth that is determined primarily by the homogeneous linewidth. Because the measured peaks X and T have similar linewidths along these two directions, either the transition energies are uncorrelated during \( \tau \) and \( t \), or the inhomogeneous and homogeneous linewidths are similar order of magnitude. Since the experiments are performed for short pump-probe delay \( t_D = 0.7 \text{ ps} \), deviation from perfect (or nearly-perfect) correlation of the linewidths is unlikely since spectral diffusion processes in semiconductors typically occur on a longer timescale. Thus, the round lineshape of the peaks implies that the
homogeneous and inhomogeneous linewidths are similar order of magnitude. This is an interesting result, since such a broad homogeneous linewidth for both $X$ and $T$, as discussed below, implies that significant pure dephasing mechanisms are present even at low sample temperature and excitation density. Under these conditions, we find negligible quantitative differences when including the effects of inhomogeneity and therefore set the inhomogeneous linewidth to zero.

$$|0⟩↔|1⟩$$

$$|2⟩↔|3⟩$$

$$|0⟩↔|2⟩$$

$$|1⟩↔|3⟩$$

<table>
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<tr>
<th>$\gamma$ (meV)</th>
<th>$\gamma_{01} = \gamma_{02} = 0.85$</th>
<th>$\gamma_{02} = \gamma_{13} = 1$</th>
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<tr>
<th>$\gamma^\text{pop}$ (meV)</th>
<th>$\gamma^\text{pop}_{11} = 1$</th>
<th>$\gamma^\text{pop}_{12} = 0.1$</th>
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<tr>
<th>$E$ (meV)</th>
<th>$E_1 = 1619$</th>
<th>$E_2 = 1651$</th>
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TABLE I. Parameter set used to produce simulated data of Fig. 3(c) in the main text. The parameters denoted with a dash are non-physical or not relevant for the experiments and simulation.

In total, the number of free parameters in the simulation equals 15, including a relative phase shift between the nonlinear signal and reflected probe and the exciton → trion population relaxation rate that is modeled by including additional decay and source terms to the Feynman diagrams. We assume that the dipole moments of the $|0⟩ ↔ |1⟩$ and $|2⟩ ↔ |3⟩$ transitions are equal (similarly for the $|0⟩ ↔ |2⟩$ and $|1⟩ ↔ |3⟩$ transitions), since the transitions originate from the same single-particle transitions. The set of parameters that are used to produce the simulated spectrum in Fig. 3(c) of the main text are shown in Suppl. Table I. The values for $E_1$ and $E_2$ are obtained directly from the trion and exciton resonance energies, respectively, in the pump-probe spectrum. The population decay rates for the trion and exciton are obtained from the exponential decay of their amplitudes with respect to the pump-probe delay $t_D$ (data not shown). The remaining parameters are determined by comparing the measured and simulated differential probe spectrum for resonant pumping at the exciton and trion resonances and using a least squares regression analysis to minimize the error. The dipole moment and homogeneous linewidth of the $|0⟩ ↔ |1⟩$ transition and the signal/probe relative phase are obtained by adjusting the parameters of this transition until the horizontal slice through peak $T$ minimizes the least squares error for this peak. A similar procedure is performed to obtain the dipole moment and homogeneous width for the $|0⟩ ↔ |2⟩$ transition (minimizing the least squares error for peak $X$).

The remaining free parameters in the simulation are associated with exciton-trion interactions, specifically EIS through $\Delta'$ and EID effects through an enhanced dephasing rate of the upper transitions. The only set of parameters that reproduces the amplitude and lineshape of peaks $XT$ and $TX$ is an EIS of state $|3⟩$ equal to $\Delta' = 4$ meV and EID of the $|1⟩ ↔ |3⟩$ transition compared to the $|0⟩ ↔ |2⟩$ transition with $\gamma' = 25$ meV. EIS is the only mechanism that produces a negative-absorptive lineshape for peak $TX$. In order to enhance the amplitude of peak $XT$ compared to $TX$, EID effects must be present. We estimate an upper and lower limit for EIS of $\Delta' = 5.5$ meV and $\Delta' = 2.5$ meV, respectively, by adjusting $\Delta'$ (and subsequently altering the other parameters to minimize the error) until the minimum least squares error increases by 50%.
